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Etching of Silicon in Fluoride Solutions

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Etching of silicon in fluoride solutions

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ABSTRACT

The development and status of what is commonly called the Gerischer mechanism of silicon etching in fluoride solutions is reviewed. The two most widely used and studied wet etchants of silicon are F^- and OH^-. Their mechanisms of atom removal share many things in common; in particular, chemical passivation by a hydrogen-terminated surface plays an important role in both. Crucially, however, their initiation steps are different, and this leads to important differences in the structures of the materials produced by the etchants. The initiation of etching by F^- is electrochemical in nature, responding to the electronic structure of the Si, and is, therefore, a self-limiting reaction that can produce nanocrystalline porous silicon. Hydroxide etching destroys porous silicon because its initiation step is a catalytic chemical reaction and not a self-limiting process. A number of unanswered questions regarding the dynamics of fluoride etching are highlighted.

1. Introduction

Gerhard Ertl's first two publications were written with Heinz Gerischer [1,2]. From a reading of these papers it would appear that it was under Gerischer's aegis that Ertl began to recognize that true dynamical understanding of elementary processes in surface reactions [3] required the establishment of an approach that had all of the rigor of the gas-phase school of chemical reaction dynamics. Ertl began by building up from the structure of the surface [4,5]. This was a necessary prerequisite that would be followed by development of the electron and vibrational spectroscopic techniques, which are required to obtain a true molecular understanding of chemical transformations on surfaces. This new school has come to be called the surface science approach. To reduce complexity and obtain the requisite rigor and reproducibility, Ertl turned away – at least at first – from the liquid/solid interface and moved to the gas/solid interface.

Coincidentally, the timeframe of their move to the University of Munich is also when Gerischer first turned to the study of the etching of semiconductors in aqueous solutions. The first studies were on germanium electrodes [6] with silicon following some years later [7]. Ertl's first surface chemical studies were also on Ge surfaces [8,9], and the two shared an interest in the elucidation of the fundamental properties of semiconductor surfaces [10]. Gerischer recognized that semiconductor electrodes provided a unique platform for the study of the dynamics of electrons and holes in electrochemical reactions [11] as well as for surface photochemical studies [12].

Studies of the electrolyte/semiconductor interface have had a profound impact on the field of electrochemistry as well as solid state physics [13]. One needs only mention the multifaceted TiO_2 [14] or its photocatalytic properties and use in Grätzel type dye-sensitized solar cells [15,16]. Semiconductors, of course, are at the heart of photovoltaic cells used for hydrogen production [17,18] or as solar cells [19,20]. Gerischer's early work on the electrolyte/semiconductor interface soon turned to studies of photoelectrochemical energy conversion, and his work lead to fundamental advances in this area [21]. It is on semiconductor surfaces that the link between electrochemistry and photochemistry was made.

The etching of silicon in fluoride is a wonderful example of how identifying reactants and products, as well as initial and final thermodynamic states, gives us no insight into surface chemical processes. What is required is a surface science approach to elucidate the dynamics. The overall corrosion reaction for Si dissolution in fluoride media under the most commonly studied conditions is given by the equation

$$Si + 6HF + h^+ \rightarrow SiF_6^{2-} + 4H^+ + H_2 + e^- \qquad (1.1)$$
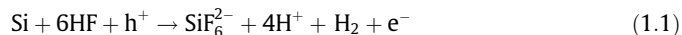
in which h^+ represents a hole injected into the valence band and an electron is injected into the conduction band. At low illumination intensities on *n*-type Si, there appears to be a second competing reaction.

$$Si + 6HF + h^+ \rightarrow SiF_6^{2-} + 6H^+ + 3e^- \qquad (1.2)$$
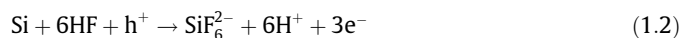
Reaction (1.1) is responsible for a process known as current doubling and Rxn (1.2) for current quadrupling. In current doubling the photocurrent quantum yield is two, that is, for each absorbed

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ns two charge carriers contribute to the measured photocurrent. In photocurrent quadrupling, four charge carriers are counted for every one photon absorbed. These simple electrochemical reactions belie a wealth of complexity in the reaction dynamics, which can only be completely understood by taking a surface science approach to the electrolyte/semiconductor interface.

First we need to recognize that fluoride solutions are themselves complex and not entirely well understood [22]. To state that HF exists either in an undissociated or dissociated form in water is an oversimplification. Instead it appears to oscillate between an undissociated form and a contact ion pair in which both H^+ and F^- are bound strongly on either side of a molecule of water [23,24]. HF(aq) contains not only solvated H^+ and F^-, but also complex ions such as HF_2^- and $H_2F_3^-$, any and all of which may be able to participate in the reaction mechanism.

Second, we need to ask why Si does not spontaneously dissolve in acidic fluoride. When kept in the dark, the etch rate of H/Si in concentrated HF, R_{dark}, is roughly 2.5×10^{12} cm^{-2} s^{-1} ($\sim$0.3 Å min^{-1}) [25–27]. In other words, unbiased and unilluminated Si is *virtually inert* in acidic fluoride solutions even though the formation of the products in Rxn (1) is thermodynamically favored. Keep in mind, of course, that fluoride solutions do spontaneously etch silica surfaces,

$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H_2O + 2H^+. \quad (2.1)$$

$$SiO_2 + 3HF_2^- \rightarrow SiF_6^{2-} + H_2O + OH^-. \quad (2.2)$$
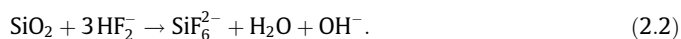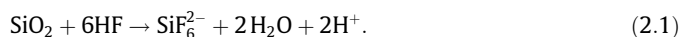
These reactions, in which HF_2^- is the more reactive of the two species [28,29], are important to recognize whenever investigating the interaction of Si surfaces with aqueous solutions because Si surfaces generally start with a native oxide film or may become covered with an oxide layer under certain conditions. While the reaction rate depends on the composition of the fluoride solution, generally the dissolution of silica is very rapid and *isotropic*. Hence, dissolution of Si appears to be kinetically hindered, whereas dissolution of SiO_2 is not.

Third, we can ask why etching in alkaline solutions leads to such different final states compared to etching in fluoride. Alkaline etching of silicon follows the reaction [30]

$$Si + 2H_2O + 2OH^- \rightarrow [Si(OH)_2O_2]^{2-} + 2H_2. \quad (3)$$
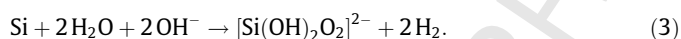
While this reaction appears to be completely different than reactions (1.1) and (1.2), we shall see below that essentially all of the steps in F^- and OH^- induced etching of Si are the same *except the crucial first step*. Because of this alkaline etching is a chemical reaction that occurs catalytically under the influence of OH^- [31]. Alkaline and fluoride etching of silicon are both *anisotropic* but in very different respects. We shall see that because of this, alkaline etching, which is much the same as the so-called chemical reaction that occurs in moderate to high pH fluoride solutions, can be used to create flat, nearly perfect surfaces, while fluoride etching can be used to form nanocrystalline porous silicon films. The versatility of fluoride etching also allows it to be used in the selective area formation of macropore arrays [32], silicon nanowires [33,34], and in micromachining [35,36].

2. Surface termination

A bare silicon surface is highly reactive and would never survive for long when exposed to either air or an aqueous solution. Silicon exposed to the atmosphere rapidly oxidizes to form a native oxide layer with a thickness of several angstroms [37]. After degreasing in solvents, when a native oxide surface is placed in a fluoride solution, Rxns. (2.1) and (2.2) rapidly remove the oxide. This is a fundamental difference between fluoride and alkaline (non-fluoride

containing) solutions. If the adsorbed hydroxide concentration becomes too high, a surface oxide condenses and soon covers the surface. In the absence of fluoride in solution, this oxide forms a passivating layer. Condensation of neighboring hydroxides into a surface oxide is also involved in other phenomena such as the observation of current oscillations during dissolution [38] or the observation of a porous silicon formation only below a critical current density with electropolishing occurring above this value [39,40].

Based on chemical intuition, it originally seemed obvious that the resulting surface should be terminated with F atoms. After all, the Si–F bond with a dissociation energy around 7 eV [41] is one of the strongest single bonds known in chemistry, and the Si–H bond dissociation energy is only around 3.2 eV [42]. This conclusion was bolstered by an erroneous determination of a F-terminated surface based on X-ray photoelectron spectroscopy (XPS) data [43]. For these reasons, the original formulation of the Gerischer mechanism, as well as those of other authors [44], were based on a F-terminated surface [13,45,46]. This only goes to prove that in surface science, even the most gifted intuition requires reliable surface-sensitive data to determine reaction dynamics.

There have been several reports of at least partial F-termination [47–51]. It is important to distinguish whether the observed F-related signal is caused by a chemisorbed species. The presence of physisorbed etch products, rather than chemisorbed reaction intermediates, is more consistent with most reports because the F-containing species is removed by a water rinse [50,52–59]. Furthermore, XPS probes the near surface region, not just the top layer. Subsurface fluorine in interstitial sites may also account for the presence of a fluorine signal [58]. *Ab initio* electronic structure calculations suggest that penetration of F into the Si lattice is a facile process [60,61]. Recent XPS data on emmersed (still coated partially with adsorbed water) Si electrodes suggest that the etching of *n*-type Si(111) in the dark with 0.1 M NH_4F at pH 4 leads to a surface covered with θ(Si–H) = 0.5 ML, θ(Si–HOH) = 0.25 ML and θ(SiHF) = 0.15 ML. Such large coverages of F and OH should easily be observed in infrared spectroscopy not only in the Si–F and Si–OH stretch regions but also because of the profound effect a neighboring electronegative species has on the Si–H stretch [62–67].

With this as a backdrop, it was a stunning result when Chabal and co-workers reported [68] that strictly surface-sensitive infrared absorption spectra revealed no evidence for Si–F bonds (nor Si–OH nor Si–O–Si) and that the surface was only terminated with H atoms. Subsequent demonstrations of essentially perfectly flat H-terminated Si(111)–(1 × 1) surfaces [69] as confirmed by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) [39,54,70] were further evidence that any steady-state concentration of F or O containing reaction intermediates is extremely small (<0.01 ML) and their presence is often determined by rinsing conditions as well as exposure to air. *In situ* measurements during etching also confirm that the Si surface is predominantly H-terminated throughout the etching process [38,71–75]. There may be a small oxygen coverage (as –OH) during etching [76]; thus, H_2O and OH^- may play competing roles to HF (or HF_2^-) and F^-, respectively, in some of the steps under some conditions. The roles of H_2O and OH^- will, of course, be enhanced by low fluoride concentration and high pH. Within the reaction schemes developed below it would be expected that there is some transient coverage of OH and F on the surface. How much the coverage of these species builds up depends on the relative rates of the initiation reaction and all subsequent steps. Oxide and hydroxyl species as well as their response to applied voltage have been observed by *in situ* infrared spectroscopy by Chazalviel and co-workers [40] in *low fluoride concentration* solutions. Their results are consistent with etching being initiated at H-terminated sites.

The observation of a H-terminated surface required a fundamental redrawing of the Gerischer mechanism, or what should perhaps be called the Gerischer mechanism revisited. This was done in the insightful work of Gerischer in collaboration with Philippe Allongue and Virginia Costa Kieling [39,78]. While the composition of the surface had to be redrawn, the underlying chemistry of the mechanism remained in tact. Indeed, the driving force for all of the steps after the initiation of the reaction – the polarization of Si–Si backbonds – explains precisely why the surface is H-terminated instead of F-terminated.

The Si–F bond is extremely polar. In comparison, the electrons in a Si–H bond are almost evenly shared. Because of this, H-termination of a Si crystal is the perfect way to trick the surface and selvage atoms into believing that they are still in the bulk. H-termination of all dangling bonds allows the Si atoms to relax and return very close to their ideal bulk-terminated positions [79]. This relieves strain, strengthens the lattice, and results in almost perfect chemical and electrical passivation of the H-terminated Si surface. On Si(1 1 1) the surface tends toward its bulk-terminated (1 × 1) structure. On Si(1 0 0), neighboring dihydride units experience an unfavorable steric interaction, which inhibits the formation of a perfect (1 × 1) structure. Instead, some roughening of the surface occurs. Nonetheless, the surface is still passivated.

The Si–F bond is so highly polar that is also polarizes the Si backbonds. This was proposed by Gerischer [45,46,78] and has been confirmed by theoretical studies [80–82]. The polarization makes these bonds labile and susceptible to chemical attack. Therefore, the reason that the surface is H-terminated instead of F-terminated is essentially a kinetic one. The presence of adsorbed F is autocatalytic for the etching reaction. Once an F atom absorbs, the subsequent steps must be very fast so that a low steady-state coverage of F(a) builds up. The reactions also have to be such that once the Si atom is removed, any dangling bonds are naturally capped with H atoms.

3. The initiation step: role of holes

The role of valence band holes in controlling anodic oxidation of semiconductors was recognized by Brattain and Garrett for Ge [83] and Uhlir for Si [84]. Beck and Gerischer [85] proved that the reaction rate on *p*-type Ge is proportional to the surface concentration of holes. Because of the different reactivities of surface electrons and holes, the doping type of the crystal leads to very different reactivities for *n*-type and *p*-type doping (see Fig. 1).

The underlying premise of Gerischer's explanation [7] for the dissolution of semiconductors under the influence of excited carriers (regardless of whether they are created by photoexcitation or by an applied bias) is that the valence band is bonding with respect to the bonds of the substrate, and the conduction band is antibonding. Therefore, the presence of a hole in the valence band reduces the strength of bonds in its vicinity and makes the substrate atoms susceptible to attack by nucleophiles. The presence of a conduction band electron, analogously, weakens bonds in its vicinity and makes those substrate atoms susceptible to electrophilic attack. Consequently, whether holes or electrons accumulate at the surface determines if the attack of nucleophiles or electrophiles is promoted. Accumulation of holes occurs under anodic bias; accumulation of electrons under cathodic bias. In the absence of a bias, band bending in the space charge region (SCR), as shown in Fig. 2 pushes holes to the surface of *n*-type Si, whereas it pushes electrons to the surface of *p*-type Si.
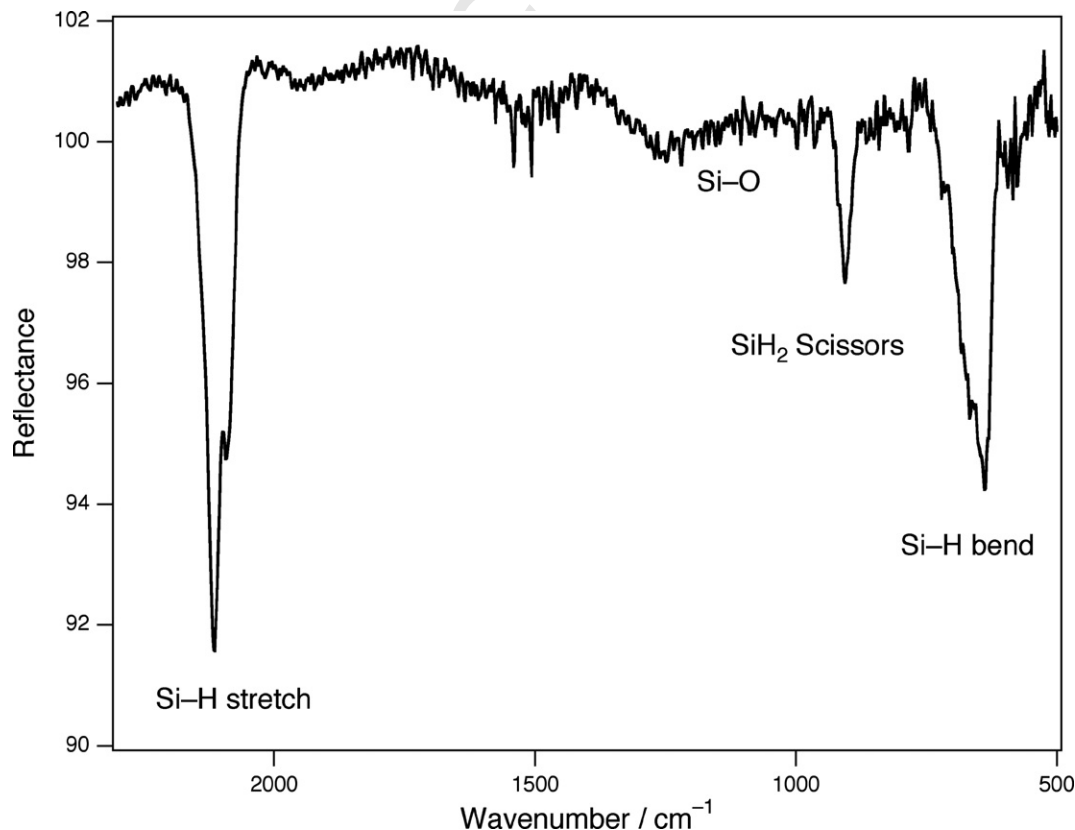

Fig. 1. Diffuse reflectance FTIR spectrum taken in air of a porous silicon layer demonstrating the overwhelming H-termination of a Si surface produced by etching in fluoride solutions even when the sample has been rinsed in water and methanol and exposed to air for >30 min. The layer was produced by stain etching of *p*-type Si(1 0 0) in a solution composed of HF + FeCl₃ + H₂SO₄ as described in [77].
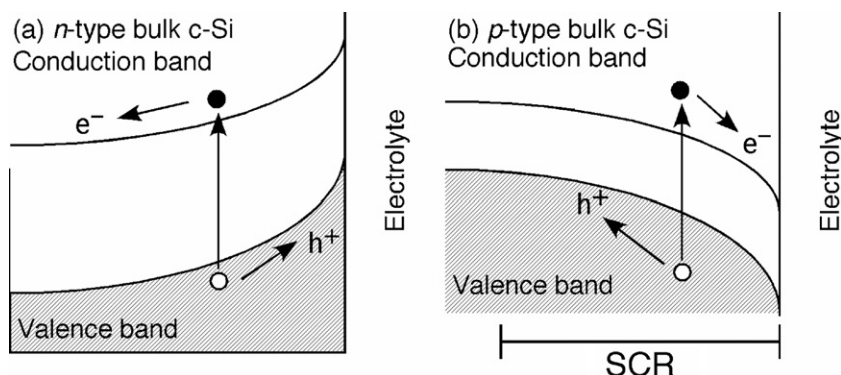
K.W. Kolasinski / Surface Science xxx (2009) xxx–xxx

Fig. 2. Band bending and the motion of electrons (e⁻) and holes (h⁺) under the influence of the space charge region (SCR), when the e⁻–h⁺ pair is made, e.g. by the absorption of a photon with an energy greater than the band gap. The SCR is that region near the surface where the bands are not flat resulting from a charge imbalance at the interface as compared to the bulk. The bands bend (a) upward in *n*-type Si and (b) downward in *p*-type Si.

Control of the initiation step is the most essential aspect of silicon etching. The need for holes at the interface ties fluoride etching to (i) the electronic structure of the silicon and (ii) the nature of hole injection. Holes can be generated by an applied bias (leading to electrochemical etching), by hole injection from an oxidant (electroless or stain etching) or by photon absorption (photoelectrochemical or laser-assisted etching depending on whether a bias is applied or not). The electronic structure of silicon is inherently controlled by the size of the silicon structures through quantum confinement. Consequently the generation and transport to the interface of holes provide feedback between etching and feature size. This feedback makes hole-initiated fluoride etching a self-limiting process that does not lead to the complete dissolution of silicon. Instead, once the features reach the nanoscale, quantum confinement passivates small structures and directs holes to the bottoms of pores rather than to pore walls [86–88]. This etching anisotropy induced by carrier transport leads to the formation of nanocrystalline porous silicon (por-Si) films.

Any other mechanism that removes the passivating H atoms, resulting in dangling bonds, will also initiate etching in a fluoride solution. First we might consider spontaneous deprotonation of the surface, as has been invoked to explain a chemical reaction at the H/Si surface [39]. To do this we calculate the Boltzmann factor, $\exp(-\Delta E/kT)$, between the H/Si surface and the deprotonated surface. The energy difference is estimated [89] to be $\Delta E = 4.74$ eV, and the Boltzmann factor is on the order of 10^{-80}. Therefore, spontaneous deprotonation from the H-terminated surface does not play a role under normal conditions.

Two species that are important for removal of H(a) are OH⁻ and dissolved oxygen. Chemical etching initiated by OH⁻ attack is highly anisotropic and occurs essentially only at step edges. Therefore, initiation by hydroxide attack leads to step flow etching and the production of atomically flat, H-terminated Si(1 1 1)–(1 × 1) surfaces, as proposed by Jakob et al. [90] and Allongue et al. [39,91,92]. After ligand exchange, chemical etching proceeds essentially in the same manner described below as etching induced by electronic excitation. Hydroxide-catalyzed hydrolysis of the surface does not require the presence of a hole. Instead it is a thermally activated process and its probability is expected to increase exponentially with temperature. The importance of hydroxide-catalyzed etching increases with pH and dominates at least by pH 8. Dissolved oxygen strongly affects the etch rate of Si in 40% $NH_4F(aq)$ solutions [93]. Etching initiated by dissolved oxygen is much less discriminating [94] than hydroxide-induced etching. It can remove chemisorbed H from either terrace or step sites, and such etching leads to more defective surfaces. Consequently, we see that by controlling the initiation of fluoride etching, we can control the structure of the material that is left behind.

4. The Gerischer mechanism step by step

The revised and improved Gerischer mechanism of silicon etching in fluoride solutions is presented in Fig. 3. This figure contains not only Steps (1) through (5a), which correspond to an improved version of the revised Gerischer mechanism, but also Steps (5b) through (7), which comprise the current quadrupling branch not included in the original model. Whether or not both branches are required and which is the dominant branch is still a question in need of resolution.

The first chemical change that occurs in the etching of Si in a fluoride solution is the replacement of a chemisorbed H atom with a chemisorbed F atom. The inertness of the H-terminated Si surface is explained by the extremely low absorption probability of F⁻ from an aqueous solution. Kolasinski has shown [89] that the sticking coefficient of F⁻(aq) on a H-terminated Si surface is <5 × 10⁻¹¹. The sticking coefficient is greater at steps than terraces [46,78,88], but even at defects it is quite small. To bring about etching at an appreciable rate, electronic excitation of the surface (or removal of adsorbed hydrogen) is required.

Steps (1) and (2) signify the formation of a hole and the transport of this hole to the surface. Like all other semiconductors with band gaps >0.5 eV, electrochemical Si dissolution requires the presence of holes at the surface [7]. However, where this hole resides can only be determined by surface science experiments that specify where the electronic states are. The hole can be generated either by an applied voltage or else by photon absorption. The use of a laser with a well-defined photon energy to initiate etching allows us to specify exactly the excitation energy and to determine which electronic states are accessible.

We know that the surface is initially H-terminated and, thus, we can use surface science experiments on the H/Si surface in vacuum to inform us. Electron spectroscopy identified [95] two surface related features on the H/Si surface. One is a surface resonance associated with the Si substrate located at −2.4 eV relative to the Fermi energy. The second is associated with the Si–H s bond and is located at −5.3 eV. In the kinetics experiments of Koker and Kolasinski [88,96,97], a HeNe laser with photons of energy 1.96 eV was used. Therefore, direct excitation of neither the state with a hole in the Si–H bond nor the surface resonance associated with the Si–Si back bond is possible. Instead, *the hole enters a bulk state and diffuses to the surface* [89]. This has important implication for how the next step of the reaction proceeds.

Direct excitation of the Si–H bond by 7.9 eV photons or by electrons from an STM tip can lead to hydrogen desorption [98]. For etching in fluoride solution initiated electrochemically, electrolessly or with visible laser irradiation, however, the Si–H bond is not directly excited and desorption of H⁺, as was suggested [39,78],
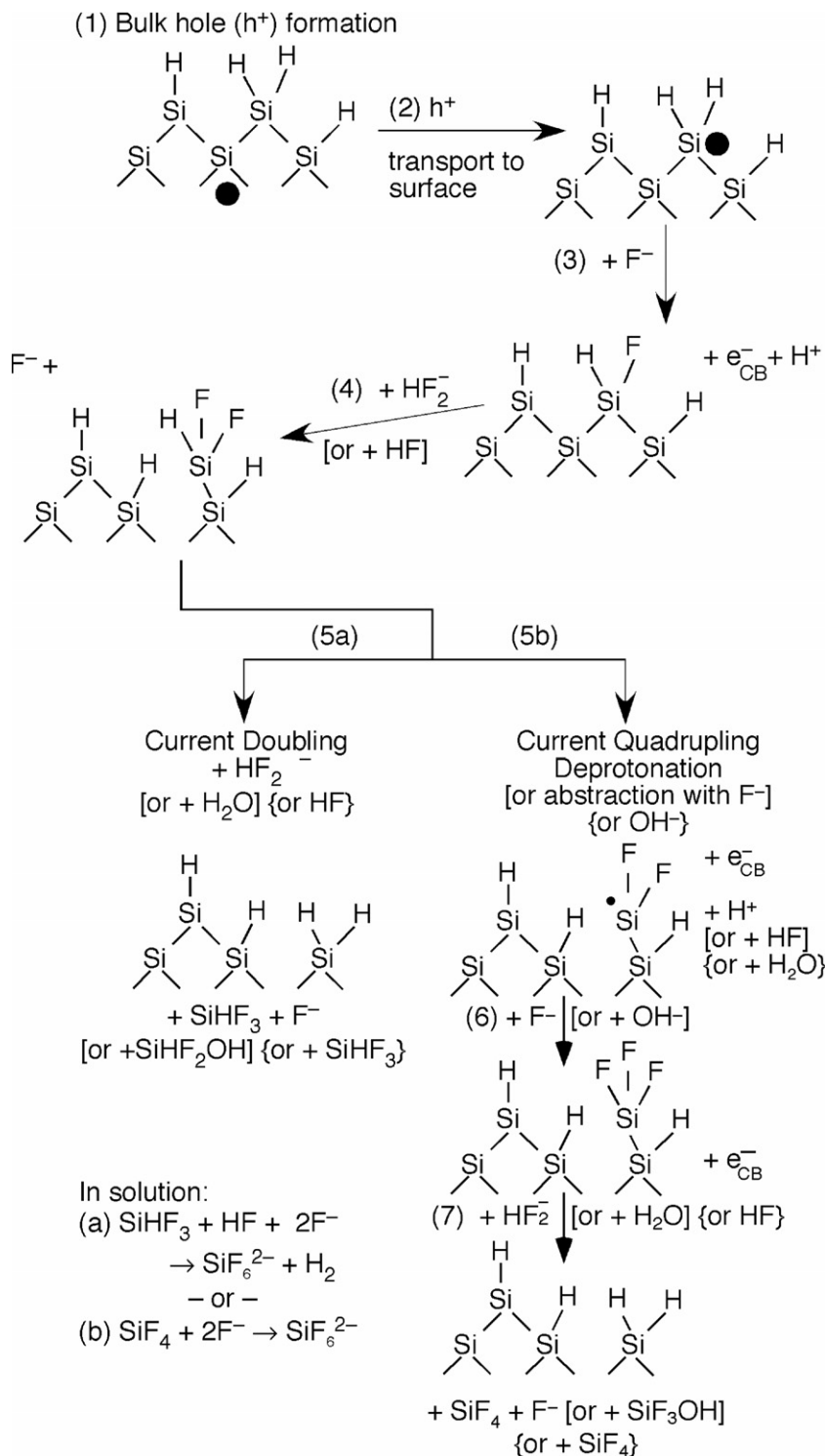
Fig. 3. The Gerischer mechanism of Si etching in acidic fluoride solutions as modified by Kolasinski [89] with important contributions from Kooij and Vanmaekelbergh [99].

is not possible. Instead, capture in Si–Si bonds occurs, akin to the suggestion of Kooij and Vanmaekelbergh [99]. Nonetheless, direct attack of the Si–Si bond does not occur, probably as the result of steric hindrance, because this would not maintain a H-terminated surface, inconsistent with experimental results [78].

This brings us to Step (3), the substitution of H(a) with F(a). Kolasinski has shown [89] that the sticking coefficient of F^-(aq) on H/Si is increased by 10 orders of magnitude by the electronic excitation. The presence of a hole causes the sticking coefficient

to approach unity. While it is still higher at steps and kinks, the sticking coefficient must also be high at terrace sites because of the observation of porous silicon formation rather than step flow etching. The requirement for etching at a kink site, as pointed out by Lewerenz and co-workers [76,100–102] is clearly a deficiency in the original model, because roughening and por-Si formation occur.

During Step (3) a hole is injected into the Si conduction band, which results in current doubling [46]. What is unclear is the

mechanism of the substitution reaction. There are two possibilities (i) abstraction of H^+ by F^- to form HF followed by absorption of F^- at the dangling bond site, or (ii) the formation of a pentavalent transition state in which both the incoming F^- and the departing H^+ are still attached to the Si that will be etched. The role of the hole in case (i) is to weaken the Si–H bond as in the classical interpretation of the Gerischer model. In case (ii) the hole acts to stabilize the transition state. The woeful lack of theoretical calculations in general and dynamics calculations in particular for the F/H/Si system leaves this question unanswered. The presence of the solution complicates these calculations. Neurock and co-workers have shown [105,106] that the solvent can play an integral role in solution/surface chemistry and advances in computational techniques are becoming increasingly capable of accounting for this.

As the pH increases, especially if the fluoride concentration is low, the OH^- catalyzed reaction will eventually be able to compete with F^- in this step. OH(a) is less polarizing than F(a) and is, therefore, less effective at promoting the subsequent steps. Consequently if OH(a) is formed in this step, it is probable that it will be replaced by and F atom. This type of ligand exchange has been invoked to explain the chemical etching of Si as mentioned above.

The rate of hole formation and transport to the solution/silicon interface determines the rate of etching. If this rate is held constant, for instance by holding the illumination intensity constant, the dependence of the etch rate on solution composition can be determined. Koker and Kolasinski [89,96] showed that the etch rate R_A is given by

$$R_A \approx [s(HF)Z_w(HF) + s(HF_2^-)Z_w(HF_2^-)]\theta_n, \tag{4}$$

where the s terms are sticking coefficients, the Z_w terms are the impingement rates and θ_n is the coverage of holes at the surface. HF_2^- is (15 ± 2) times more reactive than HF. The sticking coefficients, $s(HF) = 1.1 \times 10^{-3}$ and $s(HF_2^-) = 1.6 \times 10^{-2}$, are much greater than the sticking coefficient of F^- on H/Si in the absence of a hole but much less than the value in the presence of a hole, as required for consistency with experimental observations. It is clear that this step is branched and that HF_2^- is more reactive than HF. However, since both reagents lead to the same surface structure and composition, the consequences of this branching are kinetic rather than structural.

The requirement that the coverage of F, $\theta(F)$, is minimal, demands that all of the chemical steps after initiation are quite rapid. Once a hole arrives at the surface and reacts with an impinging $F^-(aq)$, the subsequent steps occur in rapid succession such that $\theta(F)$ does not build up. Each step is more rapid than the previous step because substitution of H(a) by F(a) polarizes the backbonds and makes them more susceptible to attack. Two substitutions make the backbonds even more susceptible to attack than does one substitution. Thus, Step (4) is the rate determining step of the chemical steps after initiation of the reaction.

It should be noted that much like OH^- can substitute for F^-, H_2O can also substitute for HF or HF_2^- in this or any other step below. Furthermore, the probability of OH^- or H_2O acting as a substitute increases with increasing pH. Recognizing this symmetry between these two sets of species, we are able to see commonality in etch characteristics that allows a unification of the mechanisms of electrochemical and chemical etching in fluoride solutions with alkaline etching. A pentavalent transition state in a reaction step equivalent to Steps (3) and (4) has been proposed for etching by OH^- [103] and has been invoked [104] to explain the anisotropy of alkaline etching. Fluoride etching following electronic excitation does not exhibit the same degree of anisotropy. Therefore, either a pentavalent transition state is not formed during fluoride etching or it does not exhibit the same degree of steric hindrance since fluoride etching does not exhibit the same degree of anisotropy.

At Step (5) is where a more meaningful branching of the reaction can occur [99], not only in a manner that affects the kinetics of etching, but also charge multiplication and the formation of H_2. Current doubling is most commonly and reproducibly observed, and it is what will be observed if Step (5a) is followed. Step (5a) is the reaction of $SiHF_2(a)$ with either HF_2^-, HF or H_2O to form the etch products of the appropriate stoichiometry and a H-terminated surface.

$$SiHF_2(a) + HF_2^- \rightarrow SiHF_3(aq) + F^- \tag{5.1}$$

$$SiHF_2(a) + HF \rightarrow SiHF_3(aq) \tag{5.2}$$

$$SiHF_2(a) + H_2O \rightarrow SiHF_2OH(aq) \tag{5.3}$$

This step is extremely rapid, and it is not known what the relative reactivities of the three reagents are. Subsequently the etch product reacts to form SiF_6^{2-} as well as H_2

$$SiHF_3 + HF + 2F^- \rightarrow SiF_6^{2-} + H_2. \tag{6}$$

Note that for each Si atom that is etched, one H_2 molecule is produced but it is not produced through a surface reaction. Instead the reaction occurs homogeneously in solution. Simple ligand substitution of F^- for OH^- in $SiHF_2OH$ to produce $SiHF_3$ will achieve the same result. One suggestion [99] is that Rxn (6) proceeds via two-step hydrolysis reaction

$$HSiF_3 + H_2O \rightarrow SiF_3OH + H_2 \xrightarrow{+HF} SiF_4 + H_2 \xrightarrow{+2F^-} SiF_6^{2-} \tag{7}$$
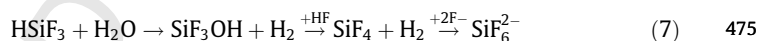
At sufficiently low light intensity, current quadrupling is observed in both aqueous [44,107–110] and nonaqueous [111] solutions. A great deal of effort has gone into explaining the transition from quadrupling to doubling, the data for which has always been analyzed under the assumption that the Gärtner equation is valid to explain the hole flux to the surface [112]. This equation assumes that bulk recombination and Auger recombination are negligible. However, what has not been recognized in these arguments is that surface recombination velocity of Si in HF(aq) is extraordinarily low [113].

The effects of Auger recombination manifest themselves when the carrier generations rate, G, approaches what is required for the Auger recombination rate to be equal to the surface recombination rate. Assuming a uniform generation rate of holes within the space charge region, the generation rate is given by

$$G = \frac{\Phi_{dl}}{W} \tag{8}$$

where

$$\Phi_{dl} = \Phi_0(1 - r_{Si})(1 - e^{-\alpha W}) \tag{9}$$

is the amount of light absorbed in a space region of width W, is the incident photon flux, r_{Si} is the reflectivity of Si and absorption coefficient. The Auger recombination coefficient is $G_p = 4 \times 10^{-31}$ cm^6 s^{-1} [114] and the Auger recombination rate (equal to $1/t_A$ the Auger lifetime) is given by

$$\frac{1}{\tau_A} = G_p p_n^2 \tag{10}$$

where p_n is the excited carrier density. For a typically doped Si crystal in HF, the surface recombination rate has an exceptionally low value of 4.5×10^3 s^{-1}. The Auger recombination rate equals the surface recombination rate, $G_p p_n^2 = 4.5 \times 10^3$ s^{-1}, when the excited carrier density reaches $p_n = 1 \times 10^{17}$ cm^{-3}. This corresponds to $G = (0.4-4) = \times 10^{18}$ cm^{-3} s^{-1}, an incident power density of 50–500 µW cm^{-2}, or equivalently a photon flux of $(0.16-1.6) \times 10^{15}$ cm^{-2} s^{-1}. This range matches the photon flux at which the current multiplication data make the transition from 4 to 2 [44,107–110]. The influence of Auger recombination on the current multiplication

data cannot be ignored – the rate of Auger recombination is competitive with the rate at which carriers are consumed in surface recombination and etching.

The observation of current quadrupling has been dogged by irreproducibility [107–109]. One question has been whether the high intensity illumination "activation" of the surface, which makes observation of the effect more likely [109], is actually due to oxidation of the surface [78]. However, the simultaneous observation that the extent of H_2 generation during etching also changes appears to corroborate that something is changing during etching at low and high illumination intensities, even if there are only a few scattered data points that point toward this behavior [107–109]. Current quadrupling and no H_2 formation are observed for fluoride etching in a nonaqueous solvent [111]. Etching in the absence of H_2 bubble formation has also been observed for fluoride etching initiated by hole injection from $Fe^{3+}(aq)$ [115]. Both of these observations lend further evidence for the existence of another branch in the etching mechanism.

Kooij and Vanmaekelbergh [99] have proposed an insightful extension to the Gerischer mechanism that can properly account for current quadrupling and a change in H_2 production. This mechanism must be further corrected [89] such that (i) the hole that initiates the reaction occupies a bulk state rather than a surface state, (ii) a steady-state H-terminated surface is generated, and (iii) the mechanism allows for the competition between HF and HF_2^-, as well as OH^- and H_2O in some steps. These corrections are embodied in Steps (5b) through 7. At Step (5b), they introduced deprotonation with concurrent injection of an electron into the conduction band and formation of a Si atom with a dangling bond,

$$SiHF_2(a) \rightarrow {}^\bullet SiF_2(a) + H^+. \tag{11.1}$$

However, simple deprotonation may be a slow and uncompetitive process – as it is in Step (3). Thus, the abstraction of H^+ by F^- or OH^- should also be considered to be a viable route until further evidence, perhaps provided by *ab initio* calculations, is able to address this point.

$$SiHF_2(a) + F^- \rightarrow {}^\bullet SiF_2(a) + HF. \tag{11.2}$$

$$SiHF_2(a) + OH^- \rightarrow {}^\bullet SiF_2(a) + H_2O. \tag{11.3}$$
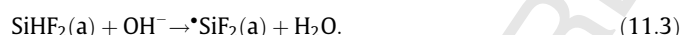
Abstraction of chemisorbed H by H atoms incident on H/Si occurs readily under UHV conditions [116]. Whether similar processes are important in solution phase interfacial chemistry is an open question. The superior ability of F^- to abstract H(a) as compared to OH^- may also help to explain some crucial differences between fluoride and alkaline etching of silicon.

Step (6) is the capping of the dangling bond with F^- and the injection of a hole into the conduction band to complete the current quadrupling. Step (7) is much like Step (5a)

$$SiF_3(a) + HF_2^- \rightarrow SiF_4(aq) + F^-. \tag{12.1}$$

$$SiF_3(a) + HF \rightarrow SiF_4(aq) \tag{12.2}$$

$$SiF_3(a) + H_2O \rightarrow SiF_3OH(aq). \tag{12.3}$$

Note [99] that the lack of an H atom in the etch product released into solution opens up the possibility of the following reaction

$$SiF_4 + 2F^- \rightarrow SiF_6^{2-}, \tag{13}$$

which does not release H_2 as required.

5. Conclusion

The development and current status of an extended and revised Gerischer mechanism of silicon dissolution in fluoride solutions

has been presented. The model is an example of how the surface science approach is essential for molecular level mechanistic understanding of etching reactions. Several concepts are key to understanding etching by both fluoride and hydroxide: (i) surface passivation provided by a H-terminated surface, (ii) the role of the initiation step in determining the rate, anisotropy, and response to electronic structure/excitation, (iii) back bond polarization induced by electronegative adatoms, (iv) similarities in the roles of $\{F^- \text{ and } OH^-\}$ as one set and $\{HF, HF_2^- \text{ and } H_2O\}$ as another set of reactants, and (v) splitting reactions in which an H atom is transferred to a surface site and the more electronegative species (F or OH) is transferred to the silicon atom that will be etched. Electronic excitation of the H-terminated Si surface increases the sticking coefficient of $F^-(aq)$ by 10 orders of magnitude and pushes etching from a regime in which either flat or rough surfaces are formed into one in which porous nanocrystalline silicon is formed. One question of great interest that has not been addressed here is that of the onset of porous silicon formation and how the dissolution of one site leads to an increase of the surface area [40,76].

While we understand a great deal about the etching of silicon a number of outstanding questions remain, such as (i) the role of abstraction reactions in Steps (3) and (5b), (ii) is a pentavalent transition state traversed in Step (3), (iii) to what extent does a transition from current quadrupling to doubling (with concurrent H_2 production) occur and what controls the branching ratio, and (iv) why is it that for fluoride the electrochemical initiation step has a rate that far exceeds the rate of catalytic water splitting whereas for hydroxide, the reverse is true. Further surface science and electrochemical experiments, as well as support from *ab initio* calculations, are required to answer these questions. It will be essential that *ab initio* calculations in the style of those of Neurock and co-workers [105,106], which more accurately take into account the role of the solution/solid interface, are undertaken to obtain an accurate portrayal of the dynamics.

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